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THE OXIDATION OF MOLECULAR TRITIUM RELEASED TO THE ATMOSPHERE

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ABSTRACT

The present state of knowledge is reviewed. The processes expected to dominate atmospheric oxidation are the gas phase reaction with the hydroxyl radical, and the biochemical oxidation occurring in soils at the atmosphere-land interface. A simple model is developed to estimate the relative importance of these two processes on a ground-level release of molecular tritium. The dependence of the rates of these processes on environmental parameters and the isotopic composition of the tritium molecule (HT, DT, or T_2) are, in general, not well understood. The conclusion is drawn that field experiments, under realistic conditions, will be necessary to generate this information.

1.0 INTRODUCTION

Tritiated water vapour is known to be approximately 2.5×10^4 times more radiotoxic than tritium in the molecular (or elemental) form (Easterly and Phillips, 1980; Martin, 1982). Hence, to determine the environmental fate and impact of a release of molecular tritium to the atmosphere, it is essential to quantify the rate at which it is oxidized within the atmospheric environment. If this knowledge were not available, it would probably be necessary to make the very conservative assumption that all the tritium released is rapidly converted to tritiated water vapour.

At present, most of the tritium released to the atmosphere by Ontario Hydro's nuclear operations is in the form of tritiated water vapour. However, it is planned to install a tritium-recovery system at the Pickering Nuclear Generating Station by the mid-1980's. During the recovery process the tritium will be converted to the molecular form. The potential thus exists for the release of this species to the atmosphere. The early generations

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of fusion reactors will also probably have large inventories of elemental tritium (∿100 MCi/reactor), hence the safety and environmental aspects of the release of elemental tritium have been identified by the Canadian Fusion Fuels and Technology Project as an important area for investigation.

This report is organized in the following manner:

Section 2.0 presents a summary of the present state of knowledge regarding the atmospheric oxidation of tritium.

Section 3.0 develops an analysis, based on a simple dispersion model, which gives an estimate of the relative importance of the major known oxidation mechanisms. An evaluation of the status of knowledge is made and recommendations for future research are given in the concluding remarks.

2.0 MAJOR OXIDATION PROCESSES

On the basis of present knowledge, two processes are expected to dominate the atmospheric oxidation of tritium (Burger, 1979; Ogram, 1982). These are the gas phase reaction with free radicals of photochemical origin and the biochemical processes occurring at the atmosphere-land interface. These are discussed briefly below.

2.1 Gas Phase Oxidation

The gas phase oxidation of elemental tritium is expected to occur dominantly through the reaction with the hydroxyl radical (Burger, 1979; Ogram, 1982).

$$OH + HT \rightarrow HTO + H \qquad (1)$$

or

$$\rightarrow H_2O + T$$

Figure 1 summarizes the photochemical cycle of relevance to the oxidation of hydrogen and its isotopes in the atmosphere. Rate coefficients are given in Table I. Note that for the reaction of OH with DT and HT either tritiated water vapour or a tritium atom may be formed (for the reaction with T_2 both are, of course, formed). This T atom is expected to react rapidly to form either tritiated water vapour, or other stable tritiated species, such as TNO_3 (Figure 1 shows some possible pathways).

The rate coefficient for reaction (1) shows a significant isotope dependence because of the large mass ratios between the hydrogen isotopes. Experimental measurements of the rate coefficients for the reaction of OH with H_2 and D_2 have been made (Smith and Zellner, 1974; Ravishankara, et al, 1981). The rate coefficients are temperature dependent. The temperature dependence is also different for each isotope. For example at T = 250 K, k_H/k_D = 5.4 ±1.5 and at 298 K, k_H/k_D = 3.3 ±0.9 where k_H and k_D are the rate coefficients for the reactions with H_2 and D_2 respectively. The rate coefficient for reaction with T_2 has been estimated in Table II using the expression given by Stern and Vogel (1981), (Ogram,1982). Table II also shows typical atmospheric lifetimes

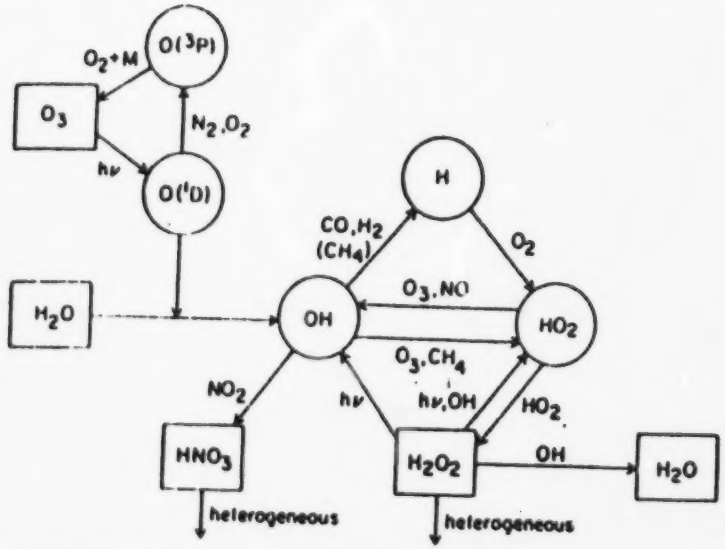


Fig. 1. Major chemical reactions affecting odd hydrogen (OH, H, HO_2, H_2O_2) in the troposphere.

(from Logan et al, 1981)

TABLE I

RATE COEFFICIENTS FOR REACTIONS OF IMPORTANCE TO ATMOSPHERIC HYDROGEN (from Logan et al, 1981; Heicklen, 1976)

Reaction	Rate coefficient* ($cm^3 s^{-1}$)
$OH + H_2 \rightarrow H_2O + H$	1.2-11 (-2200/T)
$H + O_2 (+M) \rightarrow HO_2 (+ M)$	1.5-12
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.1-14 (-580/T)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.8-14 (1250/T) x (1 + (2.5-18)$[H_2O]$)
$HO_2 + NO \rightarrow OH + NO_2$	4.3-12 (200/T)
$OH + HO_2 \rightarrow H_2O + O_2$	4.0-11
$OH + CO \rightarrow CO_2 + H$	2.7-13
$2OH \rightarrow H_2O + O$	1.0-11
$OH + CH_4 \rightarrow H_2O + CH_3$	2.4-12 (-1710/T)
$OH + O_3 \rightarrow HO_2 + O_2$	1.6-12 (-940/T)
$OH + NO_2 (+M) \rightarrow HNO_3 (+ M)$	1.3-11
$H + O_3 \rightarrow OH + O_2$	1.23-10 (-562/T)
$H_2O_2 + h\nu \rightarrow OH + OH$ $\rightarrow HO_2 + H$	
$OH + H_2O_2 \rightarrow H_2O + HO_2$	1.7-12

Isotopic exchange reactions may also be important, eg

$$T + H_2O \rightarrow HTO + H$$

$$T + H_2O_2 \rightarrow HTO_2 + H$$

*The notation a-b (-c/T) is read as a x 10^{-b} exp (-c/T)

TABLE II

ISOTOPIC DEPENDENCE OF THE RATE COEFFICIENT FOR THE REACTION

$$H_2 + OH \xrightarrow{k} H_2O + H$$

	$k(cm^3s^{-1})$		k_{H_2}/k		τ_{chem}(years) $= (k[OH])^{-1}$
	T = 25°C	T = 0°C	T = 25°C	T = 0°C	T = 25°C
H_2	$6.08(\pm0.37)\times10^{-15}$	3.32×10^{-15}	1	1	5.2
HD					
HT					
D_2	$1.83(\pm0.12)\times10^{-15}$	6.39×10^{-16}	3.3±0.9 (expt.)	5.2	17.2
DT					
T_2			6.6 (est)	13.3 (est)	35

↑ Expected Order of Decreasing Reactivity

↑ Experimental results of Ravishankara et al (1981)

↑ For $[OH]_{av} = 10^6 cm^{-3}$ (daytime max can be $\gtrsim 10^7 cm^{-3}$)

Branching Ratios

$HT + OH \rightarrow H_2O + T$ Light Atom Transfer Favoured

or $\rightarrow HTO + H$

($\tau = (k[OH])^{-1}$) for some of the isotopic species against reaction with atmospheric OH. These lifetimes are calculated using a value of $[OH] = 10^6 cm^{-3}$, which represents a nominal, diurnal average concentration at ground level, in an unpolluted atmosphere (Logan et al, 1981).

The series of reactions responsible for the formation of OH in an unpolluted atmosphere are initiated by the photodissociation of O_3 by solar ultraviolet (UV). The chemical lifetime of OH in the atmosphere is very short and it is found that the steady state OH concentration follows the intensity of solar UV flux closely, (Logan et al, 1981; Heicklen, 1976). The hydroxyl concentration reaches a maximum at midday and falls off to negligible levels at night. Measurements and photochemical model studies indicate that in polluted atmospheres daytime maximum values may be as high as $4x10^7$ cm^{-3} (eg, Campbell et al, 1982).

In summary then, the gas phase oxidation of molecular tritium at any point within the atmosphere at a particular time would be expected to depend, at least, on the following factors:

- ambient temperature

- solar intensity (which depends on time of day, altitude, latitude, season and extent of cloud cover)

- presence of pollutants which may enhance the formation of OH (eg, O_3, NO_2 and hydrocarbons)

- the isotopic composition of the tritium molecule (HT, DT or T_2).

The "average" tropospheric lifetimes against reaction with OH quoted in Table II, range from about 5 years for H_2 to an estimated 35 years for T_2 (for a nominal [OH] of 10^6 cm^{-3}). It is apparent, however, from the above discussion, that the rate of conversion may, on occasion, be expected to be more than an order of magnitude greater than these values, giving much shorter chemical lifetimes.

Mason (1977) has derived a value for the chemical lifetime of HT in the troposphere of 6-10 years. This value was obtained by fitting measured global HT concentrations between 0 and 14 km altitude to a simple continuity model.

For comparison, atmospheric lifetimes of H_2 derived from chemical kinetic models range from about 2 years to 10 years (eg, Levy, 1973; Logan et al, 1981).

The radioactive decay of tritium, of course, gives an effective upper limit on the chemical lifetime of the T_2 molecule (Burger, 1979). The process is:

$$T_2 \xrightarrow{\beta^-} HeT^+ \rightarrow He + T^+$$

$$\text{or} \rightarrow He^+ + T$$

The tritium atom or ion formed would be expected to react rapidly to form tritiated water vapour or other tritiated species by similar mechanisms to those discussed earlier. The lifetime

against this process is given by $\tau = [2\tau_{rad}]^{-1} = 8.57$ years where τ_{rad} is the lifetime against radioactive decay.

2.2 Biochemical Oxidation

The other significant pathway that has been demonstrated is the biochemical oxidation of elemental tritium by microbial action within soils, (McFarlane et al, 1978; Garland and Cox, 1980). In comparison, uptake and conversion by vegetation seems to be much slower. This rate has been shown to vary with such parameters as soil moisture content, pH and temperature. A significant problem in describing the effect of this process on an atmospheric plume of molecular tritium is that one has to quantify the rate at which the elemental tritium is brought into contact with the soil. This may be conveniently parameterized by a deposition velocity v_d defined such that the flux of tritium to the soil for oxidation is given by the product $N\ v_d$ where N is the concentration of molecular tritium in the atmosphere above the soil.

Values of v_d obtained or estimated from the literature are given in Section 2.3, together with a critical description of the experimental techniques used. In Section 2.4 a simple expression for v_d is derived in terms of more basic parameters. Section 2.5 discusses the fate of tritiated water vapour as formed by in-soil processes at the atmosphere-land interface and by gas phase processes within the atmosphere.

2.3 Experimental Measurements of the Deposition Velocity of Tritium to Soils for Oxidation

There are two basic procedures which have been previously used. These are described below.

The first technique involves a closed volume V, with an initial concentration of T_2 (equal to $[T_2]_0$) and area of exposed soil A, with soil depth d, (eg, McFarlane et al, 1978; Garland and Cox, 1980; Sweet and Murphy, 1981). The rate at which T_2 is oxidized is equal to the flux of T_2 to the soil for oxidation multiplied by the area of the soil exposed to the air in the chamber. That is

$$\frac{d([T_2]V)}{dt} = -v_d\,[T_2]\,A \qquad (2)$$

Equation (2) has the solution:

$$[T_2] = [T_2]_0\ \exp\ (-v_d\ tA/V) \qquad (3)$$

v_d is thus given by the slope of a semilog plot of $[T_2]$ versus time. If only two measurements are available (initial concentration at $t = 0$ and concentration at a later time $t = t'$) then

$$v_d = \ln\ (\ [T_2]_0/[T_2](t'))\ \ V/At' \qquad (4)$$

In the second type of configuration (eg, Sweet and Murphy, 1981) a constant concentration of T_2 in air is flowed over a soil sample. The total amount of tritium deposited to the soil and oxidized is equal to the product of the flux, soil surface area and the elapsed time. The deposition velocity is thus given by

$$v_d = \frac{\text{Total tritiated water in soil}}{[T_2]\, A\, t} \qquad (5)$$

Previous experimental results are summarized in Table III.

TABLE III

VALUES OF V_d (HT) FROM THE LITERATURE

V_d (cm s^{-1})	Method	Reference
0.001 to 0.03	Lab. experiments on incubated soil samples	McFarlane et al, (1978)
0.2	For deposition to soil and vegetation. Model fit to environmental measurements after a release of HT	Murphy and Pendergast, (1979)
0.03	Field chamber exposures	Sweet & Murphy (1981)
0.02-0.13	Lab. experiments (with flow vel. 0 to 1.5 m s^{-1}	Sweet and Murphy, (1981)
0.0096-0.11	Field chamber exposures to various soils (v_d decreases as soil moisture increases)	Garland and Cox, (1980)
4×10^{-5}	To Scots pine	Garland and Cox, (1980)
5×10^{-4}	To seawater	Garland and Cox, (1980)

It can be seen that measured values for various soil types under various conditions vary from about 10^{-3} to 10^{-1} cm s^{-1}. Limited information suggests that the environmental parameter most strongly correlated with deposition velocity is the soil moisture content. The deposition velocity increases as the soil becomes drier. The reason for this is thought to be that the diffusion of HT into the soil is inhibited by the presence of moisture. Results in the UK seem to indicate also that the deposition velocity does not depend strongly on the soil temperature in the range 1 to 20°C (Garland and Cox, 1980).

It is possible that some of the deposition velocities given in Table III are too low, because of insufficient depth of soil in the experimental chamber (see next section). This, however, would not influence the field measurements where the chambers were mounted on skirts driven into the soil, thereby exposing a sample of intact soil.

The rather high value for v_d of 0.2 cm s^{-1} attributed to Murphy and Pendergast (1979) in Table III was estimated from environmental measurements of tritiated water in the atmosphere and in soil and vegetation for routine releases of tritium in the form of both molecular tritium and tritiated water. Measurements were also made of tritiated water vapour in soil after a large release of molecular tritium. The deposition velocities estimated are considerably higher than those measured directly. The model developed by Murphy and Pendergast (1979) is available within Ontario Hydro (Ontario Hydro, 1981), however, because it seems to use unreasonably large values for the deposition velocity of molecular tritium results obtained from the model should be used with caution. The model does not explicitly account for gas phase oxidation.

2.4 Relationship Between Deposition Velocity and the In-soil Conversion and Diffusion Rates

The actual deposition velocity of molecular tritium to the soil for oxidation may be expressed as the reciprocal of the sum of two "resistance" terms, describing the aerodynamic resistance to atmospheric transport and the effective resistance to uptake by the soil (eg, Slinn, 1978).

$$\text{ie, } v_d^{-1} = R_{atm} + R_{soil} \qquad (6)$$

It is intuitively expected that R_{soil} will depend, firstly, on the rate of reaction within the soil, k_s, and secondly on the rate of diffusion of molecular tritium into the soil with an effective diffusion coefficient D_s).

In this treatment, the assumption that $R_{atm} << R_{soil}$ is made. It will be seen later that typically $v_d^{-1} >> R_{atm} \sim 1$ s cm^{-1}, so that this assumption is justified.

We assume also that the concentration of molecular tritium is maintained at an essentially constant value, $N(z=0)$, at the soil surface. An approximate upper limit to v_d can then be derived. The following continuity equation describes the soil concentration profile of molecular tritium. The sign convention that the vertical coordinate z is positive in the downwards direction is used in this instance for convenience. The reaction is assumed to be first order in N.

$$\frac{dN}{dt} = D_s \frac{d^2N}{dz^2} - k_s N \qquad (7)$$

We consider here the simple case where D_s and k_s have constant values (ie, do not vary with depth z).

For a steady state $\frac{dN}{dt} = 0$, and the solution of equation (7) is

$$N = N(z=0)\ \exp\left[-\sqrt{k_s/D_s}\ z\right]$$
$$= N(z=0)\ \exp\left[-z/z_e\right] \qquad (8)$$

where

$$z_e = \sqrt{D_s/k_s}$$

and is the vertical distance in which N falls off to 1/e of its value at the soil surface.

The flux at the soil surface is given by

$$J\Big|_{z=0} = -D_s \frac{dN}{dz}\Big|_{z=0} \qquad (9)$$
$$= v_d\ N(z=0)$$

by the definition of deposition velocity.

It follows from equations (8) and (9) that

$$v_d = \sqrt{k_s D_s} = k_s z_e = D_s/z_e \qquad (10)$$

In this analysis we have assumed that D_s and k_s are constant, at least to the depth of significant penetration of HT. If we assume that the biochemically active layer is limited to a depth of d then for $d >> z_e$, as above

$$v_d = k_s z_e \qquad (11)$$

and for $d << z_e$ it can easily be shown by simple mass conservation considerations that

$$v_d = k_s d \qquad (12)$$

The first expression thus gives an upper limit for v_d.

The diffusion coefficient for molecular tritium in soils may be estimated by the following empirical formula (Jacobs et al, 1980).

$$D_s = \frac{D_{\text{gas phase}} \times \text{porosity}}{\text{tortuosity}} \qquad (13)$$
$$= D_{\text{gas phase}} \times \frac{0.2}{1.5}$$

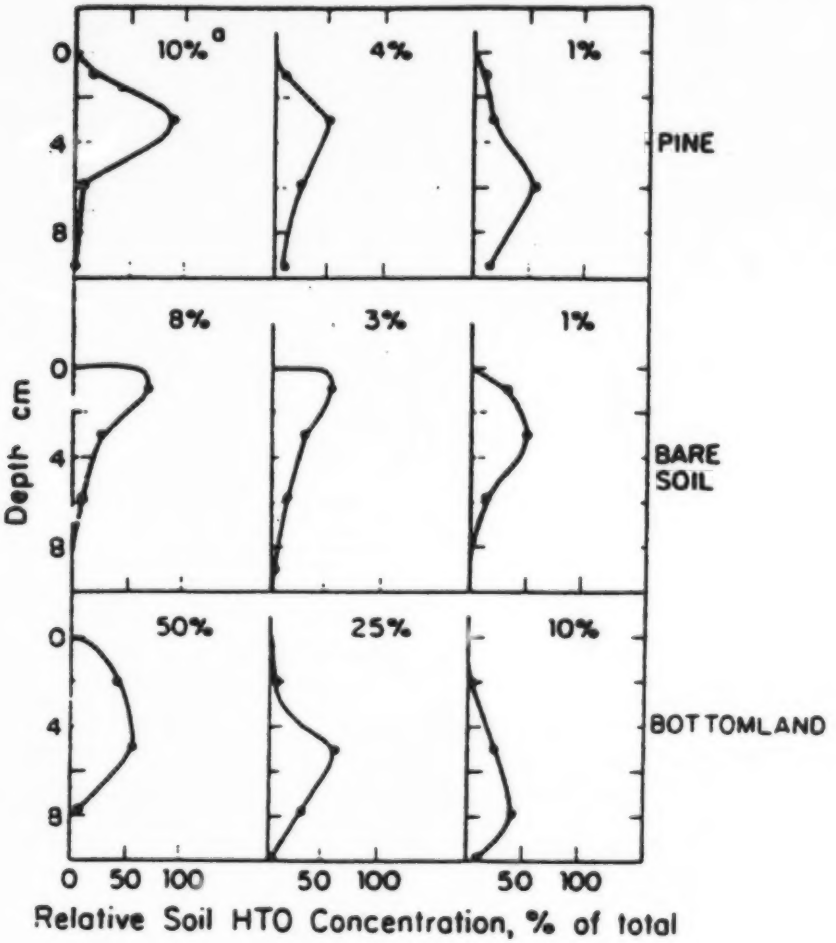
This gives approximate values for D_s of 0.056, 0.051 and 0.045 $cm^2\ s^{-1}$ for HT, DT and T_2 respectively.

Experimentally measured tritium deposition profiles can be compared with the above expression to get some idea of the validity of the above treatment.

Figure 2 shows deposition profiles measured by Sweet and Murphy (1981). The two left-hand profiles for the case of bare soil seem to show an approximately exponential fall off in tritium concentration with depth in the soil. The fall off distance z_e is

FIGURE 2

(from Sweet and Murphy, 1981)



[a]Soil moisture content, 0-5 cm depth

Effect of moisture levels on tritium deposition profiles.

about 3 cm which, using (10), implies a v_d of 0.02 cm s^{-1}. The experimentally measured v_d ranged from 0.019 to 0.031 cm s^{-1}, for the conditions shown. This is in good agreement with the result derived above using the simple model put forward here.

Note that from comparison of equations (11) and (12), it appears that it is important to ensure that the depth of the soil sample is greater than z_e when carrying out experimental measurements of v_d, otherwise a spuriously low deposition velocity will be measured. This point was raised earlier in the discussion of experimental techniques.

2.5 The Fate of Tritiated Water Vapour Formed by the Oxidation of Atmospheric Molecular Tritium

It is apparent that the tritiated water vapour formed by gas phase processes and by biochemical activity at the atmosphere-soil interface may have significantly different fates and hence impact. In the first case, gas phase oxidation, the tritiated water vapour is distributed through the lower atmosphere in a similar way to the molecular tritium precursor, provided that the altitude profile of OH is reasonably constant. Tritiated water vapour formed by this process could therefore be expected to be treated in the same way as a direct release of tritiated water vapour. That is, it would be dispersed by atmospheric winds and diffusion, and be removed from the atmosphere by dry and wet deposition. The eventual sink for most of the tritiated water vapour formed would be loss, by dilution, to the oceans (Ogram, 1982).

The question arises as to whether the fate and impact of tritiated water vapour formed by the oxidation of elemental tritium in soils is significantly different from that of tritiated water vapour formed by gas phase reactions.

Considerable study has been carried out on the fate of tritiated water applied to soil (eg, Metteinen, 1979). The results of these studies are summarized briefly here. Rates of downward transport and soil residence time depend strongly on soil type and moisture content. Typically, however, two residence "half lives" are seen, one of the order of 1 to 10 days in duration and another of 100 to 1 000 days. The first time constant applies to tritium in the upper layers of the soil where evaporation and transpiration may rapidly return it to the atmosphere. In the deeper layers the longer lifetime is apparent.

Biochemical activity is only expected to be important in the top few cm of soil (see Section 2.4), hence one would expect most of the tritiated water vapour formed by this process to be returned to the atmosphere on a time scale of approximately 1 to 10 days. A possible exception to this would be the effect of rainfall which is likely to carry the tritiated water to the deeper layers of soil before it can be returned to the atmosphere by evaporation and transpiration.

Typical average drainage rates observed on the application of a pulse of labelled water are 1 m a^{-1} for fine soils. Measured drainage velocities range from $\sim$2 cm day^{-1} for very wet soils to $\sim$0.1 cm day^{-1} or less for dry (desert) soils.

3.0 THE RELATIVE EFFECT OF GAS PHASE AND BIOCHEMICAL OXIDATION PROCESSES ON AN ATMOSPHERIC RELEASE OF MOLECULAR TRITIUM AT GROUND LEVEL

As discussed earlier, biochemical and gas phase oxidation are expected to be the dominant oxidation mechanisms for molecular tritium in the environment. It is conceivable, but not demonstrated, that other processes may be of significance (eg, surface catalyzed reactions on particulates and other surfaces). A simple analysis of the relative effects of the gas phase and biochemical processes on the oxidation of a ground-level release of molecular tritium to the atmosphere, is presented below. Because the biochemical conversion occurs at the atmosphere-land interface, the concentration of tritium in the atmosphere above the soil surface needs to be known to evaluate the net conversion rate. A simple dispersion model is used to calculate this. No particular accuracy or merit is claimed for the model chosen; it is used only for illustrative purposes and was chosen for convenience in calculation.

To calculate the fraction of molecular tritium oxidized by biochemical processes, as a function of the distance of plume travel, we use the standard approach for calculating source term depletion due to deposition (eg, Miller et al, 1978; McKone, 1978). The flux of molecular tritium to the ground for oxidation at any point is

$$J(x,y) = v_d N(x,y,o) \qquad (14)$$

where v_d is the deposition velocity of molecular tritium to the ground for oxidation, which we assume to be the same at all points, and $N(x,y,o)$ is the atmospheric concentration of molecular tritium at ground level. Mass balance considerations can be used to show that the rate of change of the effective source term for the plume, Q, due to plume depletion at a particular distance x' is given by:

$$\left.\frac{\partial Q(x)}{\partial x}\right|_{x'} = -\int_{-\infty}^{\infty} J(x',y)\, dy \qquad (15)$$

Upon substitution of equation (14) into (15) and using the expression for $N(x,y,o)$ for a Gaussian plume (eg, McKone, 1978), the integration of the resulting equation leads to the following expression. This treatment assumes that the functional form of $N(z)$ is not significantly changed by deposition. A necessary condition for this is that the deposition velocity is much less than a typical atmospheric transfer velocity.

$$Q(x) = Q \exp\left[-\left(\frac{2}{\pi}\right)^{1/2} \frac{v_d}{u} I(x)\right] \qquad (16)$$

where u is the average wind speed (assumed to be in the x direction) and $I(x)$ is given by

$$I(x) = \int_o^x \left[\sigma_z(x')\right]^{-1} dx' \qquad (17)$$

where σ_z is the standard deviation of the plume in the vertical direction. The fractional amount F(x) of the plume deposited to the ground for oxidation is equal to 1 - (the fraction remaining in the plume = Q(x)/Q(o)). Thus

$$F(x) = 1 - \exp\left[-\left(\frac{2}{\pi}\right)^{1/2} \frac{v_d}{u} I(x)\right] \quad (18)$$

which can be approximated by

$$F(x) \simeq (2/\pi)^{1/2} \frac{v_d}{u} I(x) \quad (19)$$

if the exponent is small (ie, small plume travel distance).

The standard deviation of the vertical distribution, σ_z, needs to be specified. Two choices were made for the purposes of this analysis. Both were taken from the literature and chosen for their simple (analytically integrable) power law functional form (ie, $\sigma_z = ax^b$). They are shown in Figure 3. Also shown, for comparison, are the standard Pasquill curves (eg, Turner, 1970). As can be seen, the σ_z chosen give some idea of the effect of varying the range of atmospheric stability. To avoid the singularity in I(x) at x = 0, σ_z (x=0) was chosen to have a finite value (10 m and 30 m respectively). $\sigma_z(x)$ was therefore given by $\sigma_z(x) = a(x + \alpha)^b$ where α was chosen to make $\sigma_z(0)$ = 10 or 30 m. This formalism implies that the plume is in contact with the ground at its point of origin with vertical dimension of the order of the building height. This is probably a fairly realistic assumption because of building wake effects.

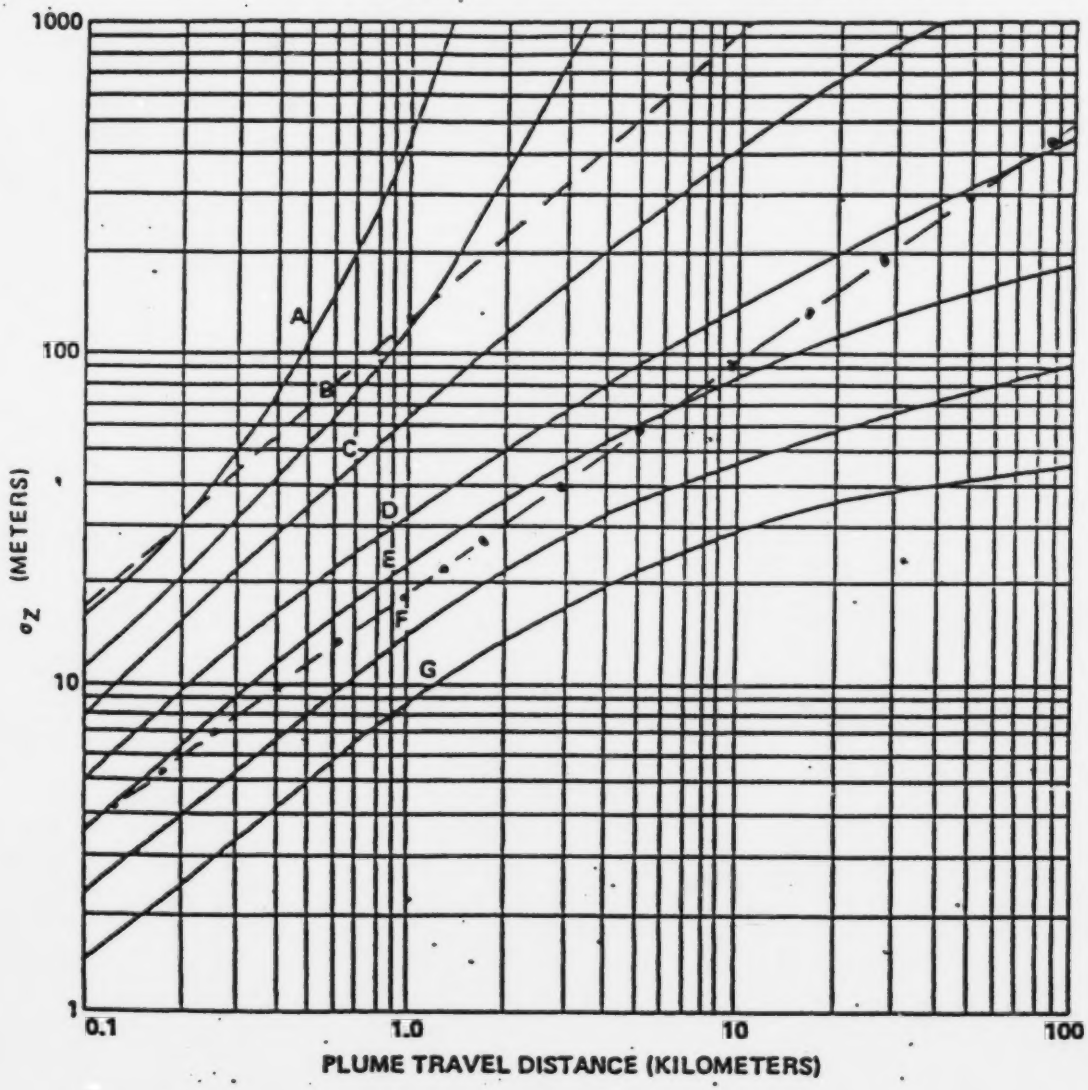
The vertical dispersion is assumed to increase with plume travel distance until it reaches 0.8 L, where L is a mixing layer height, and then remain constant at that value thereafter. This procedure for taking into account the effect of plume trapping within the boundary (or mixing) layer was suggested by Turner (McKone, 1978). It has obvious drawbacks in dealing with the diurnal variation in mixing layer height, for example, however, it should give an approximate idea of the effect of plume trapping.

For comparison, the fractional amount of tritium oxidized by photochemical processes needs to be calculated. The gas phase reaction is first order in the concentration of molecular tritium. The total amount of tritium oxidized due to gas phase reaction is, therefore, independent of tritium concentration (which is affected by dispersion) and dependent only on the time of travel of the plume. If we assume that [OH] is constant, then the amount of molecular tritium present in the plume will decay exponentially with plume travel time, t = x/u, with an exponential time constant $\tau = (k\,[OH])^{-1}$ where k is the rate of reaction of molecular tritium with the OH radical. We have also implicitly assumed that the temperature is constant throughout the plume, as the rate coefficient is expected to be temperature dependent. The fraction, F(x), of

FIGURE 3

(Adapted from Ontario Hydro, 1981)

SIGZ = 0.33 $x^{0.86}$ — — — — (Murphy & Pendergast, 1980)
=0.15 $x^{0.70}$ — • — • — (McRone, 1978)



Vertical Standard Deviation of Material in a Plume (Letters denote Pasquill Stability Class)

the plume converted to tritiated water vapour at a plume travel distance x is equal to the fraction of molecular tritium remaining subtracted from unity. That is

$$F(x) = 1 - \exp(-t/\tau)$$

$$= 1 - \exp(-x/u\tau) \qquad (20)$$

If the exponent is small, the above equation may be approximated by

$$F(x) \simeq \frac{x}{u\tau} \qquad (21)$$

A problem arises in making an appropriate choice of τ. As indicated earlier in Section 2.1, Mason (1977) derived an average value of the tropospheric lifetime of HT of $\gtrsim$6 years. The effective first order rate is thus chosen as τ^{-1} = 1/6 year^{-1} = 5.28 x 10^{-9} s^{-1} for purposes of this comparison.

Figure 4 shows for comparison, the fraction of HT oxidized for the cases of gas phase conversion only and biochemical conversion only. The fraction converted is multiplied by the factor 2.5×10^4 to give some idea of the radiotoxic impact of the tritiated water formed as compared to that of the molecular tritium remaining in the plume. As can be seen, the impact of the tritiated water formed exceeds that of the remaining molecular tritium typically after a few km (or less for the higher ranges of deposition velocity). Figure 4 also shows that the fractional amount converted by biochemical processes is very sensitive to v_d. It can be shown that F(x) is reasonably approximated by equations (19) and (21) for the range of values of F(x) shown in Figure 4. Hence by equation (19) the fractional amount converted is linearly dependent on the value of v_d, in the case of biochemical conversion only.

Figure 5 shows the effect of varying the vertical dispersion (ie, σ_z), the initial value of $\sigma_z(x)$ and the mixing layer height, on the fraction oxidized by the biochemical process. Note the considerable sensitivity to these parameters, especially $\sigma_z(x=0)$. The effect of this parameter is large because ground-level concentrations are relatively much higher near the source and changes in these concentrations significantly affect the fraction oxidized.

It can be seen that the effect of biochemical oxidation appears to be significantly greater than gas phase oxidation provided that the plume is in contact with the ground and the deposition velocity is greater than about 10^{-2} cm s^{-1}. The above analysis is expected to give an effective upper limit on the effect of biochemical conversion as the plume is assumed to be always in contact with the ground and the plume is assumed to retain a Gaussian profile with maximum concentrations occurring at ground level.

For a plume fully mixed in the boundary layer, the effect of biochemical oxidation can be expressed as a simple first order reaction with an effective rate coefficient (eg, Garland and Cox, 1980).

$$k_{biochem} = v_d/L \qquad (22)$$

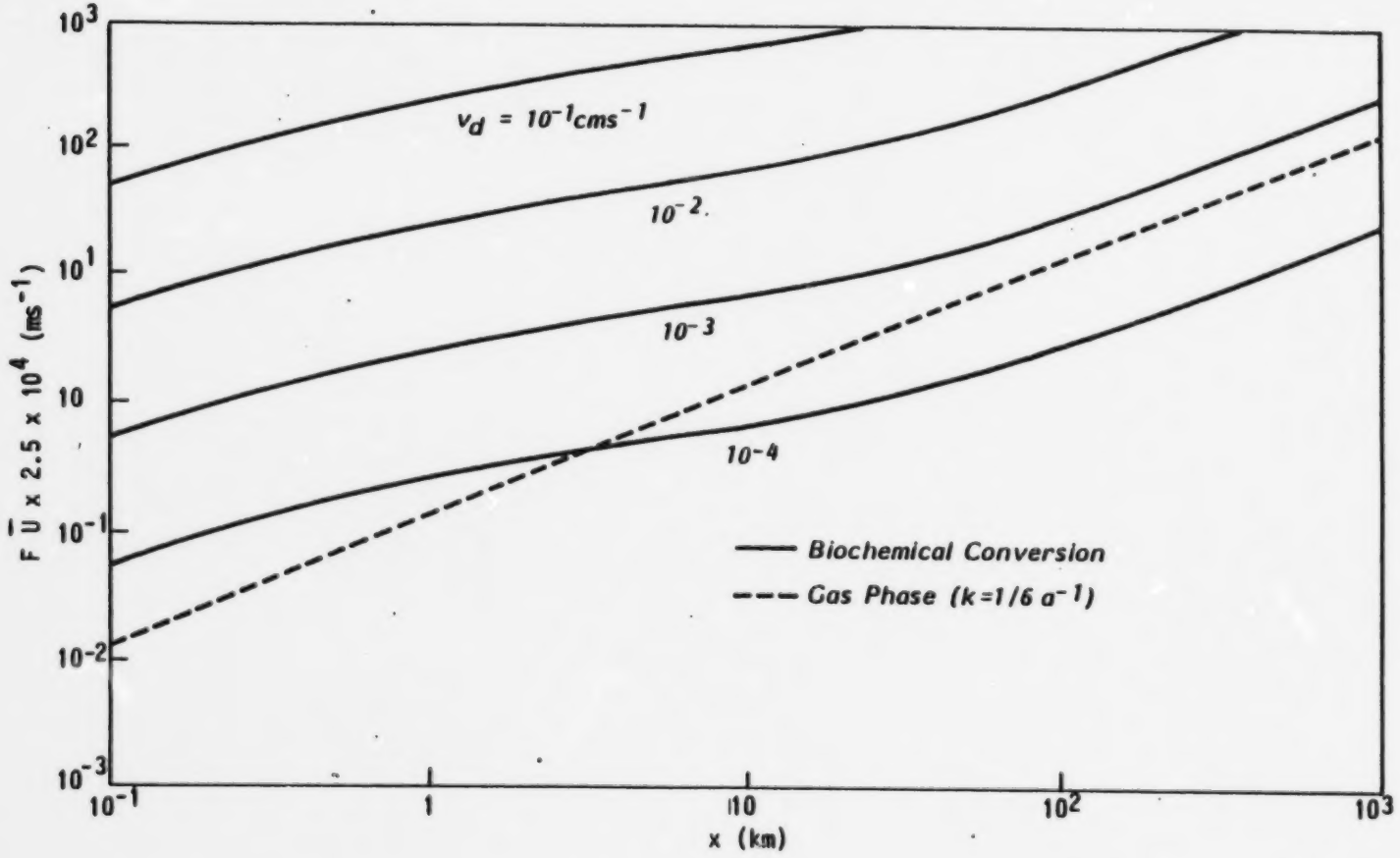


FIGURE 4

F(x) (FRACTION OF HT OXIDIZED) x $\bar{U}$ x 2.5×10^4 VS DISTANCE TRAVELLED BY PLUME $\sigma_z = 0.33\ x^{0.86}$, σ_z (x=0) = 30 m

159893 RD

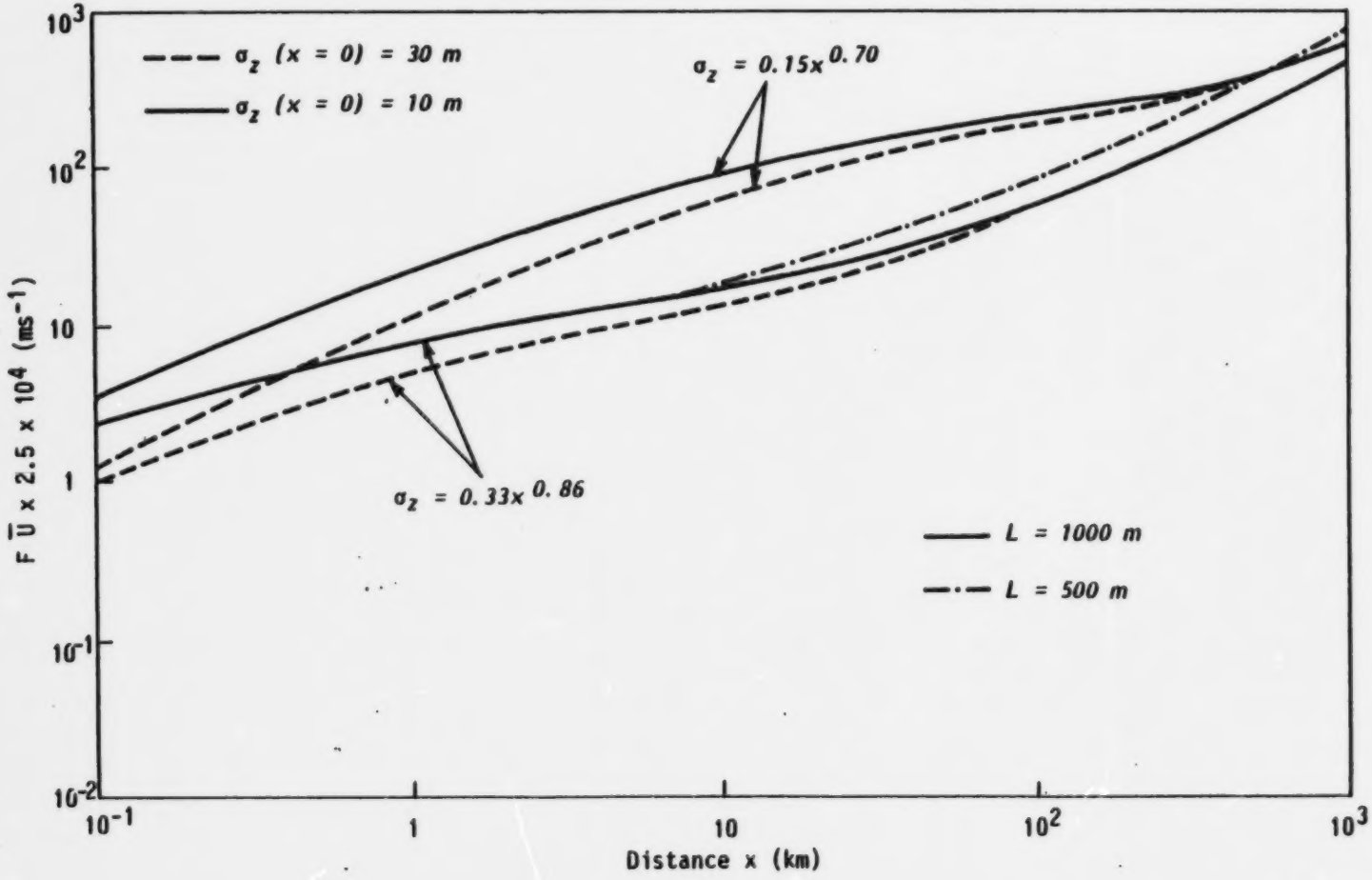


FIGURE 5

F(x) (FRACTION OF HT OXIDIZED) x $\bar{U}$ (WIND SPEED) x 2.5 x10^4 VS DISTANCE SHOWING EFFECT OF VERTICAL DISPERSION, σ_z, AND MIXING LAYER HEIGHT L, v_d = 2 x 10^{-3} cm s^{-1}

159894 RD

This gives, for example, for L = 1 000 m, the values for $k_{biochem}$ of $1x10^{-9}$ s^{-1} and $1x10^{-6}$ s^{-1} for $v_d = 10^{-4}$ cm s^{-1} and $v_d = 10^{-1}$ cm s^{-1}, respectively. This compares with the (order of magnitude) estimate of a gas phase conversion rate of $5.8x10^{-9}$ s^{-1}. For comparison, the rate for radioactive decay is $1.79x10^{-9}$ s^{-1}.

4.0 CONCLUDING REMARKS

The analysis carried out in Section 3.0, together with the experimental values of tritium deposition velocity given in Section 2.0, would seem to indicate that for ground-level releases of molecular tritium, biochemical oxidation will, in general, be more significant than gas phase oxidation.

However, on the basis of present evidence, it is not possible to be certain that this would always be the case. Some conditions which may lead to very low effective deposition rates are suggested below:

- plume entrainment above the ground
- ground cover by snow
- frozen ground
- plume passage over water

Little information exists regarding the effects of the last three factors. In addition, the effect of the isotopic composition of the tritium molecule (ie, HT, DT or T_2) on the uptake and conversion rate has not been investigated and may be significant.

It is concluded that, at present, insufficient evidence exists to accurately quantify the rate of oxidation and hence consequent impact of molecular tritium released to the atmosphere. It is also concluded that even though the lifetimes against these processes are long, the effect of conversion on radiological impact is important because of the large difference in radiotoxicity between molecular tritium and tritiated water. The most effective method of developing the necessary information regarding atmospheric conversion processes and their dependence on environmental parameters, would probably be to carry out experimental measurements under realistic (ie, field) conditions. Such experiments are at present being planned.

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POOR

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